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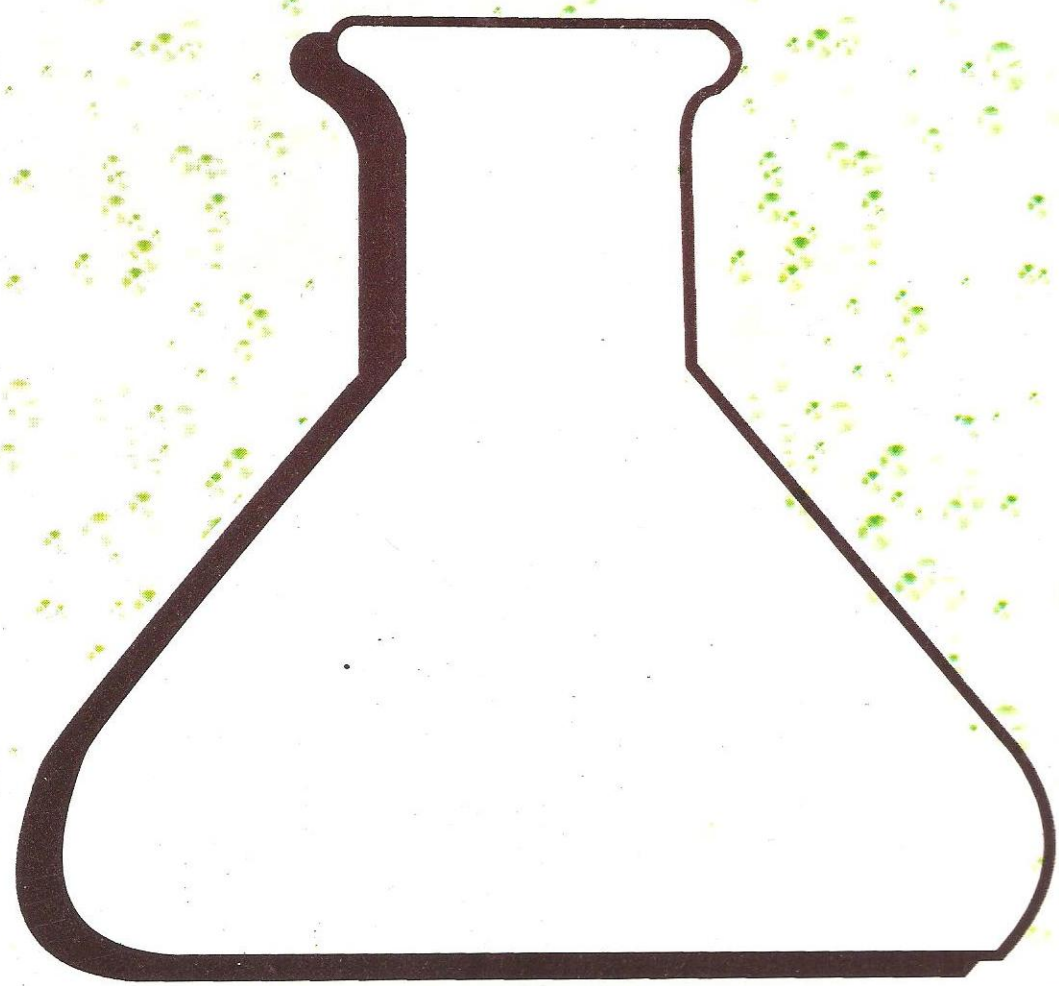

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Synthesis and Characterization of Mn^{2+} and Fe^{2+} Complexes of Potentially N4O3 Heptadentate Ligand and Antimicrobial Screening of the Complexes

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ABSTRACT

Tris-2-aminoethylamine was condensed with 5-bromosalicylaldehyde to yield the potentially heptadentate N4O3 ligand, the ligand synthesis was followed by complexation with metal ions (M= Fe^{2+}, Mn^{2+}). The complexes were characterized by infrared and UV visible, while their melting point, solubility and conductivity were investigated. The ligand C=N band appear at 1645 cm^{-1} while the C=N band infrared absorption vibration appears at 1622 cm^{-1} and 1626 cm^{-1} for iron and manganese complexes respectively. The UV absorption bands appear at low wavelengths, that is 420nm for manganese and 480nm for iron complex. Anti microbial screening on the complexes revealed that the monometallic complexes were active in inhibiting microbial growth.

Keywords: Iron, Manganese, Multidentate, Schiff base

Introduction

Schiff bases are molecules that generally possess nitrogen donor atoms. The presence of functional group such as –OH, –SH or NH_2 close to the azomethine group assists in the formation of a five or six membered ring (chelate) with the metal ion. Thus the stability of the complex can be increased by chelate effect. Schiff bases formed from salicylaldehyde and its derivative meets this requirement (Mustapha and Reglinski, 2013). The common structural feature of this compound is the azomethine group, structurally known as RR – C = NR -, where R, R - and R - are alkyl or aryl substituents or hydrogen at the point of attachment to the imino (C=N) carbon or nitrogen. Two classes of imines based on the R group attached to the azomethine groups are aldimines and ketimines. Aldimines are compounds in which R is alkyl or aryl and R - is hydrogen; while ketimines are compounds in which both R and R - are alkyl or aryl. Schiff base ligands derived from ketones are formed less readily when compared to those derived from aldehydes (Zhang *et al.,* 1999).

Schiff base transition metal complexes are one of the most adaptable and thoroughly studied systems. They are of both stereochemical and magnetochemical interest due to their preparative accessibility, diversity and structural variability. Various classes of Schiff base, derived from salicylaldehyde and primary amines are very popular due to diverse chelating ability (Viwas *et al.,* 2010). Multidentate Schiff base ligands can bind one, two, or more metal centers involving various coordination modes and allow successful synthesis of homo and/or heteronuclear metal complexes with interesting stereochemistry. Many of such complexes find application as homogeneous or heterogeneous catalysts (Radecka-paryzek *et al*., 2005).

Recently Mustapha *et al.* (2011) reported the synthesis of iron complex with hydrogenated N4O3 (donor atoms) ligand. The flexible tris-(2-hydroxybenzyl)-aminoethylamine (H6TrenSal) ligand used employ the apical nitrogen and three phenolate ions to form distorted octahedral structure. This trend was earlier observed by liu *et al.* (1993), in their report for the synthesis of $[(H6Tren5ClSal)Al]^+$ one of the secondary amine of the pendant arms was found dangling and was protonated to form mono cationic complex which is counter balanced by perchlorate anion.

Most of the multidentate ligands utilize salicylidine arms (OH in this case) to generate a neutral monomeric species, where the metal is fully encapsulated within an octahedral environment *viz* N3O3 donor atoms, avoiding the engagement of the apical nitrogen, thus remain hexadentate. This mode of coordination has been confirmed by the use of an unusual form of phosphorus tripodal ligand (Colombo-Kather *et al.,* 1994). The metal (II) reported in their paper was coordinated in distorted octahedral fashion while the apex phosphorus remain uncoordinated. The complexes formed by this nature of coordination (N3O3) are found to be very stable and can allow their usage in biology under physiological condition. Evans *et al.*

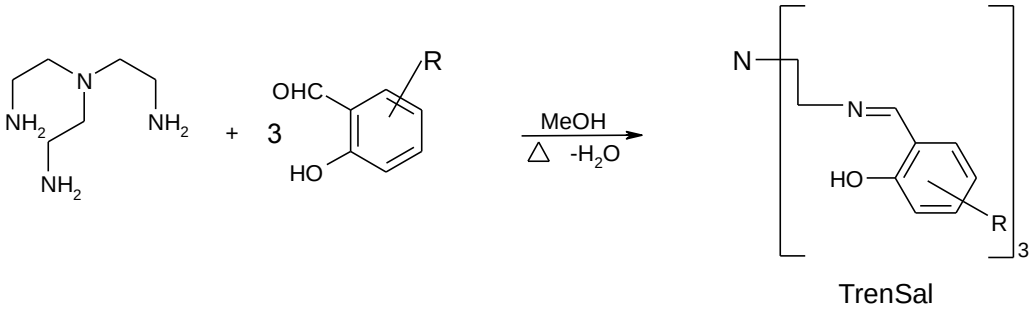
(1988) reported the study of stability constant of various Schiff base metal complexes *viz* Ni^{II} and Zn^{II}. The binding strength at particular pH (pM) values obtained revealed that the complexes affording N3O3 are more stable than those with N4O3 coordinating sites. Thus in this study, we employ the use of metal (II) ions in order to reflect the N3O3 (donor site) usage of the ligand.

Materials and Methods

All experiments were carried out using standard apparatus and commercially available chemicals. Infrared spectra ware recorded using FTIR-8400S shimadzu as potassium bromide discs. UV – visible spectra was recorded on T60 UV-visible spectrophotometer. The micro organisms used for this study were obtained from the biology department laboratory of Umaru Musa Yar'adua University Katsina (UMYUK). The organisms used are; *Stapyloccocus aureus* and *Aspergillus nigar*.

Preparation of tris-((2-hydroxy-5-bromobenzylidine)-aminoethyl) amine TrenSal

3mol equivalent of the 5-bromosalicylaldehyde (9.248g) were mixed with 1mole equivalent of tris(2-aminoethyl)amine (2.235g) in 100 cm^3 ethanol. The resulting solution was refluxed for 1 hour, filtered when hot and allowed to cool whereupon copious amounts of yellow crystals formed. These were collected and allowed to cool (Mustapha *et al.,* 2008).



TrenSal

Figure 1: TrenSal (N4O3) Ligand synthesis scheme

Preparation of tris-((2-hydroxy-5-bromobenzylidine)-aminoethyl) amine iron (II)

2.008g of the ligand (Trensal) was dissolved in 50cm^3 absolute ethanol, followed by the addition of 0.5745g of $FeCl_2.4H_2O$ and 5 drops of NaOH to the mixture. The mixture was refluxed for 3 hours after which the solution was allowed to cool and a dark purple solid filtered and dried, yield 92%. (Mustapha *et al.,* 2008).

Preparation of tris-((2-hydroxy-5-bromobenzylidine)-aminoethyl) amine Manganese (II)

1.033g of the ligand tris-((2-hydroxy-5-bromobenzylidine)-aminoethyl) amine was dissolved in 50cm^3 absolute ethanol, followed by the addition of 0.294g of $MnCl_2$. $4H_2O$ and five drops of NaOH to the mixture. The mixture was refluxed for 3 hours after which the solution was allowed to cool and a dark-purple solid filtered and dried 88% (Mustapha *et al.,* 2008).

Preparation of the Culture Medium

Potato Dextrose Agar (PDA) (19.5g) was weighed by the use of electronic top loading balance, distilled water (500 cm^3) was also measured using graduated measuring cylinder. The measured distilled water was poured in borosilicate glass beaker and the measured potato Dextrose Agar was dissolved in it. The mixture was heated over a Bunsen burner flame with continuous stirring until it comes to boil The heat was turned off as soon as it boiled while the hot agar was poured into a clean conical flask. The mouth of the conical flasks containing the media were plugged with cotton wool and placed in an autoclave. The media was sterilized at 121°C for 15minutes. After sterilization, the conical flasks were removed and cooled to 50°C. The medium was then poured into sterile Petri dishes and allowed to solidify before inoculating. The same procedure was carried out using Nutrient Agar to test the bacterial isolate. (Anacona *et al., 200*5*)*

Antimicrobial Activity Tests

a. Disk method

Using sterile inoculation wire loop, bacterial colony was picked from the Test isolate aseptically from the plate and was streaked on the labelled Petri dish containing nutrient agar. Two disks one containing the concentrated complex and the second disk as a negative control were picked and placed on the labelled Petri dish using sterile forceps. The procedure

was repeated for the remaining Petri dishes respectively. Small portion of the fungal colony was picked and placed at the centre of the PDA plates by the use of inoculating needle while the disks were placed 2 cm each away from the inoculum. The inoculated fungal plates were incubated at room temperature for 1-3 days while bacterial plates were incubated at 37^{o}C for 24 hours. The appearance of growth was recorded as activity and non- activity also the zone of inhibition was noted (Mitscher, 1982)

b. Pouring Method

To the prepared media, 1ml from each of the serially diluted complex or the Schiff base were pipetted using a sterilized syringe and transferred into sterilized petridishes followed by the addition of the potato dextrose agar media, the plate were allowed to solidify before inoculating the fungal isolate. The plates were kept at room temperature for 3 days, and the fungal activities were noted. The same procedure was carried out for the bacterial isolate using 28g of the nutrient agar in1000cm^3 of distilled water.

Results and Discussion

The synthesis of the two complexes was straight forward, thus the ligand was directly reacted with the metal salt in the mole ratio of 1:1. The products were collected as powders and washed with ether. The complexes were found to be very stable with respect to heat, as their decomposition temperature were 276°C and 287°C for iron and manganese complexes respectively as against for the ligand 145.7°C. The synthesis of potentially heptadentate ligand (Figure 1) was carried out successfully; from the infrared data of the synthesized ligand indicate the formation of the azomethine group which is the fundamental feature of the targeted Schiff base, at 1638cm^{-1}. The infra red band obtained for the ligand corresponds to what has been reported earlier 1645cm^{-1} (Mustapha *et al* 2008). The C=C aromatic stretching vibration band was found at 1483cm^{-1} while the C-O band was at 819cm^{-1}. The C=N band infrared absorption vibration appears at 1622cm^{-1} and 1626cm^{-1} for iron and manganese complexes respectively as against the ligand C=N band which is 1645 cm^{-1} .

The very intense bands at low wavelengths 420nm for manganese and 480nm for iron complex, have been assigned to charge transfer transition, the aromaticity of the complexes makes the occurrence of the bands at longer wavelengths, as expected from the higher aromaticity of the ligands which eases delocalization of electron density. On the other hand, the observed new shoulder at 475nm in manganese complex spectra can be likely ascribed to an intermolecular electron transition.

Table 1: Results of solubility test of the complexes and the ligand

COMPOUNDS	ETHANOL	CHLOROFORM	BENZENE	ETHER	n-HEXANE	ACETONE	WATER
Schiff Base	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble
FeTrenSal	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble
MnTrenSal	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble

The solubility test carried out on the complexes are reported in Table 1, while the test carried out on the complexes ability to conduct electricity reveals that the compounds do not conduct (0.04 and 0.00mS at 25°C, for iron and manganese complexes respectively). These complexes do not conduct as they are neutral compounds. The metal complex is in +2 oxidation state while the ligand two pended arms from the phenolate groups were deprotonated to coordinate to the metal ion counter balancing the metal +2 oxidation state. From these data and our previous report (Mustapha *et al.*, 2010) we conclude that the complexes reported here are monomeric, with the metal iron sitting in an N3O3 octahedral environment. These types of complexes were never subjected to antimicrobial screening in the past (Mustapha and Reglinski, 2013), as such this will be their first application in the area of biology.

Table 2: Size of Inhibition (mm)

COMPLEXES	ISOLATES	CONCENTRATION (μg/ml)					
		10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	PC
MnTrenSal	*S. Aureus*	-	4	8	14	16	-
	A. Niger	-	5	10	14	15	Na
MnTrenSal	*S. Aureus*	-	5	9	15	16	-
	A. Niger	-	8	12	17	18	Na

The anti microbial activity of the two compounds revealed the compounds to be active against *Aspergillus niger*. There is no much gap difference of size of inhibition between the complexes, where they demonstrate similar trend as the concentration decreases (Table 2). No activity was recorded for the concentrations below $10^{-1}\mu$g/ml.

Conclusions

The complexes were synthesized and characterized based on the available facilities; and they were monometallic with the metal sitting in an octahedral environment. The complexes were subjected to anti microbial screening, their ability to inhibit the growth of microorganisms was a success to this study. At very low concentration the complexes were not very active as observed at $10^{-1}\mu$g/ml. Compounds activity may be enhanced by modifying the substituted group on the phenyl ring, for example introducing sulphoxide group instead of bromine, this could be our feature work.

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